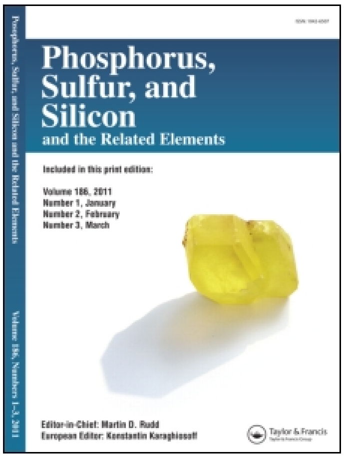

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PREPARATION AND CHARACTERIZATION OF 1-ARYLAZO-SUBSTITUTED NAPHTHYLSULFIDES

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Communication

PREPARATION AND CHARACTERIZATION OF 1-ARYLAZO-SUBSTITUTED NAPHTHYLSULFIDES

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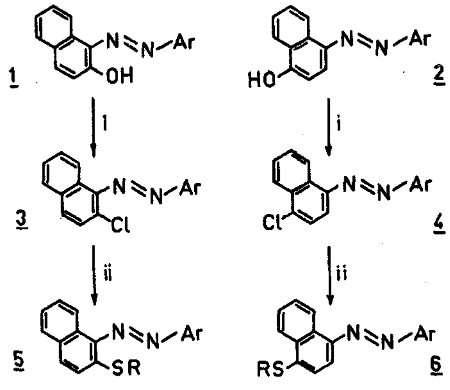
By reaction of 2-chloro- and 4-chloro-1-arylazo-napthalenes **3** and **4** with mercaptides in a dipolar aprotic solvent, stable 1-arylazo-substituted 2- and 4-naphthylsulfides **5** and **6**, resp., are formed. The hitherto unknown compounds are deeply coloured and, in many cases, considerably soluble in weakly polar organic media.

Key words: Chloronaphthalenes, 1-arylazo-substituted; nucleophilic substitution on; naphthylsulfides, 1-arylazo-substituted; order parameters of; dichroic ratio of; spectral data of.

INTRODUCTION

A large variety of naphthylazo compounds, as their benzenoid analogs, are well-known.[1] Due to their easy availability by means of a simple coupling reaction of an aryldiazonium salt with a suitable naphthalene derivative, most of them are hydroxy or amino substituted and, therefore, of deep colour. Contrary to these compounds, mercapto-substituted naphthylazo derivatives are as yet unknown. Only a few S-alkyl- or S-aryl-substituted derivatives of the parent mercapto compound are known.[2] The main reason for this seems to be that the usual coupling reaction for preparing arylazo compounds is not, in general, applicable for the synthesis of arylazo-substituted thionaphtholes. It is known, that the reaction of 1- or 2-thionaphthole with aryldiazonium salts, similar to the reaction of aryldiazonium salts with thiophenol,[3] yields very unstable arylazo sulfides which split off nitrogen during their preparation or isolation procedure. Only with highly reactive diazonium salts it is possible to couple simple S-alkyl-substituted 1-thionaphthiols. In this case, 4-arylazo-substituted 1-naphthyl-sulfides are formed.[2]

An alternative route for preparing sulfur-containing arylazo naphthols should be the nucleophilic substitution of halogen in chloro-substituted arylazo-naphthalenes by sulfur nucleophiles, analogous to the well-known preparation of nitro-substituted phenyl- or naphthyl sulfides.[4] Unfortunately, this method has not been used for preparing the desired azo compounds because the halogen-substituted educts necessary for this transformation are virtually unknown. Recently, however, we have found a simple route for preparing arylazo-substituted chloro-naphthalenes of the general formulae **3** and **4**. They are prepared from the easily available arylazo-substituted 1- and 2-naphthols **1** and **2**, resp., by transforming them by reaction with $POCl_3$ in the presence of dimethylformamide.[5]



i : $POCl_3$/DMF
ii : R-SH

SCHEME

As shown recently,[6] the 1-arylazo-substituted 2-chloro- or 4-chloro-naphthalenes **3** and **4**, resp. are usually free of further electron-donating groups, and therefore, highly reactive towards nucleophilic reagents, especially toward nitrogen compounds, such as primary and secondary amines or azide ions.

Studying the properties of the arylazo-substituted chloro-naphthalenes **3** and **4**, we recognized their reactivity towards nucleophilic sulfur compounds, especially toward alkyl- and arylmercaptans.[7] In this contribution we report in more detail on our results obtained in this direction.

RESULTS AND DISCUSSION

1. Preparation of 1-arylazo-substituted 2- and 4-naphthylsulfides 5, 6

The reaction of the arylazo-substituted chloro-naphthalenes **3** and **4** with alkyl- or arylmercaptans can be achieved by heating the components in an aprotic dipolar solvent, such as dimethylformamide or acetonitrile, preferably in the presence of a tertiary amine as proton scavenger and at temperatures of about 80–100°C. The reaction gives rise to the formation of 1-arylazo-substituted 2- or 4-naphthylsulfides **5** or **6**, resp., in mostly satisfactory yields, as shown in Tables I and II.

Similar to previous findings in reactions of the arylazo-substituted chloro-naphthalenes **3** and **4** with nitrogen nucleophiles,[6] the substituents in the aryl moiety as well as the structure of the azoeducts distinctly influence the halogen substitution by mercaptans. Actually, electron acceptor groups in the aryl moieties, such as nitro or cyano groups, promote the halogen substitution and give rise to high yields of the products **5** and **6**. Alternatively, pronounced electron donator groups, like the methoxy group, restrain the halogen substitution widely, so that these derivatives can not serve as educts for preparing appropriately substituted arylazo-substituted naphthylsulfides **5** or **6**.

Generally, 1-arylazo-substituted 4-chloro-naphthalenes **4** more uniformly form the desired 1-arylazo-substituted 4-chloro-naphthalenes **6**, whereas the isomeric 1-

TABLE I

Results of the transformation of 1-arylazo-2-chloro-naphthalenes 3 into 1-arylazo-2-naphthylsulfides 5 obtained by means of variant B

No.	Ar	R	React.-time(h)	Yield(%)
5.1	4-NO_2-C_6H_4	n-C_4H_9	12	50.5
5.2	4-NO_2-C_6H_4	n-$C_{12}H_{25}$	13	49.0
5.3	4-NO_2-C_6H_4	C_6H_5	14	40.5
5.4	4-NO_2-C_6H_4	C_6H_5-CH_2	13	47.5
5.5	2-CN-4-NO_2-C_6H_3	n-C_4H_9	12	50.5
5.6	2-CN-4-NO_2-C_6H_3	n-$C_{12}H_{25}$	12	50.0
5.7	2-CN-4-NO_2-C_6H_3	C_6H_5	14	49.5
5.8	2-CN-4-NO_2-C_6H_3	C_6H_5-CH_2	14	49.5
5.9	2,4$(NO_2)_2$-C_6H_3	n-C_4H_9	14	50.0
5.10	2,4$(NO_2)_2$-C_6H_3	n-$C_{12}H_{25}$	13.5	53.5
5.11	2,4$(NO_2)_2$-C_6H_3	C_6H_5	14	50.0
5.12	2,4$(NO_2)_2$-C_6H_3	C_6H_5-CH_2-	11	50.0
5.13	4-Cl-C_6H_4	n-C_4H_9	11	44.5
5.14	4-Cl-C_6H_4	n-$C_{12}H_{25}$	14	43.0
5.15	4-Cl-C_6H_4	C_6H_5	14.5	40.5
5.16	4-Cl-C_6H_4	C_6H_5-CH_2	15.0	40.0

TABLE II

Results of the transformation of 1-arylazo-4-chloro-naphthalenes **4** into 1-arylazo-4-naphthylsulfides **6** obtained by means of variant A

No.	Ar	R	React.-time(h)	Yield(%)
6.1	4-NO_2-C_6H_4	n-C_4H_9	12	54.0
6.2	4-NO_2-C_6H_4	n-$C_{12}H_{25}$	13	53.5
6.3	4-NO_2-C_6H_4	C_6H_5	14	51.0
6.4	4-NO_2-C_6H_4	C_6H_5-CH_2	13	56.5
6.5	2-CN-4-NO_2-C_6H_3	n-C_4H_9	12	61.0
6.6	2-CN-4-NO_2-C_6H_3	n-$C_{12}H_{25}$	12	55.0
6.7	2-CN-4-NO_2-C_6H_3	C_6H_5	14	56.0
6.8	2-CN-4-NO_2-C_6H_3	C_6H_5-CH_2	14	59.5
6.9	2,4(NO_2)$_2$-C_6H_3	n-C_4H_9	14	56.0
6.10	2,4(NO_2)$_2$-C_6H_3	n-$C_{12}H_{25}$	13.5	59.5
6.11	2,4(NO_2)$_2$-C_6H_3	C_6H_5	14	60.0
6.12	2,4(NO_2)$_2$-C_6H_3	C_6H_5-CH_2-	11	57.0
6.13	4-Cl-C_6H_4	n-C_4H_9	11	48.0
6.14	4-Cl-C_6H_4	n-$C_{12}H_{25}$	14	48.5
6.15	4-Cl-C_6H_4	C_6H_5	14.5	47.0
6.16	4-Cl-C_6H_4	C_6H_5-CH_2	15.0	46.5

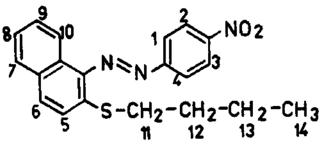
arylazo-substituted 2-chloro-naphthalenes **3** frequently give a mixture of products from which the desired 1-arylazo-substituted 2-naphthyl-sulfides **5** can be separated advantageously by column chromatography instead of a simple filtering procedure sufficient for the isolation of the 1-arylazo-substituted 4-naphthylsulfides **6**.

It is worth mentioning that, unlike the reaction with mercaptides, the arylazo-substituted chloro-naphthalenes **3** and **4** do not react successfully with the simple hydrosulfide ion. No doubt, a reaction takes place, but a definite reaction product could not, as yet, be isolated. Chromatographic checking of the reaction mixture reveals, however, the formation of a variety of products. These are probably formed by a redox reaction, since elementar sulfur could be detected among the reaction products.

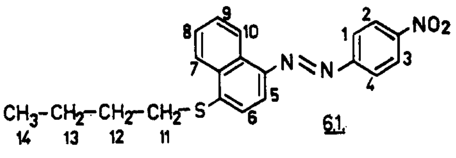
CHART I

^{1}H-NMR chemical shifts of the 1-(4-NO_2-phenylazo)-2- and 4-butyl-mercapto-naphthalenes **5.1** and **6.1**, resp., (measured in DMSO-D_6 relatively to Tetramethylsilane)

^{1}H-	/ppm				
5.1	H-1	7.98	6.1	H-1	7.98
	H-2	7.19		H-2	7.19
	H-3	7.19		H-3	7.19
	H-4	7.98		H-4	7.98
	H-5	7.38		H-5	8.29
	H-6	7.96		H-6	7.18
	H-7	7.93		H-7	9.28
	H-8	7.46		H-8	7.86
	H-9	7.68		H-9	7.71
	H-10	8.90		H-10	8.53
	H-11	2.53		H-11	2.51
	H-12	2.23		H-12	2.20
	H-13	1.65		H-13	1.64
	H-14	1.10		H-14	1.10



5.1



6.1

TABLE III

Melting points and UV/VIS-absorption spectral data of the prepared 1-arylazo-2-naphthylsulfides **5**

No.	Ar	R	m.p. (°C) (lit.)	max (nm) (lg ε)
5.1	4-NO_2-C_6H_4	n-C_4H_9	191	520 (4.28)
5.2	4-NO_2-C_6H_4	n-$C_{12}H_{25}$	241.5	521 (4.28)
5.3	4-NO_2-C_6H_4	C_6H_5	230-32	507 (4.23)
5.4	4-NO_2-C_6H_4	C_6H_5-CH_2	147-49	510 (4.26)
5.5	2-CN-4-NO_2-C_6H_3	n-C_4H_9	241-43	563 (4.31)
5.6	2-CN-4-NO_2-C_6H_3	n-$C_{12}H_{25}$	249-51	570 (4.32)
5.7	2-CN-4-NO_2-C_6H_3	C_6H_5	259	561 (4.26)
5.8	2-CN-4-NO_2-C_6H_3	C_6H_5-CH_2	188	555 (4.29)
5.9	2,4(NO_2)$_2$-C_6H_3	n-C_4H_9	281	550 (4.30)
5.10	2,4(NO_2)$_2$-C_6H_3	n-$C_{12}H_{25}$	199	552 (4.31)
5.11	2,4(NO_2)$_2$-C_6H_3	C_6H_5	180-82	537 (4.28)
5.12	2,4(NO_2)$_2$-C_6H_3	C_6H_5-CH_2-	176-77 (175-176)[2]	536 (4.29)
5.13	4-Cl-C_6H_4	n-C_4H_9	238	459 (4.21)
5.14	4-Cl-C_6H_4	n-$C_{12}H_{25}$	247	460 (4.23)
5.15	4-Cl-C_6H_4	C_6H_5	285	453 (4.19)
5.16	4-Cl-C_6H_4	C_6H_5-CH_2	253	450 (4.19)

TABLE IV

Melting points and UV/VIS-absorption spectral data of the prepared 1-arylazo-4-naphthylsulfides **6**

No.	Ar	R	m.p. (°C) (lit.)	max (nm) (lg ε
<u>6.1</u>	$4\text{-}NO_2\text{-}C_6H_4$	$n\text{-}C_4H_9$	275-78	517 (4.27)
<u>6.2</u>	$4\text{-}NO_2\text{-}C_6H_4$	$n\text{-}C_{12}H_{25}$	212	518 (4.27)
<u>6.3</u>	$4\text{-}NO_2\text{-}C_6H_4$	C_6H_5	222-24	503 (4.25)
<u>6.4</u>	$4\text{-}NO_2\text{-}C_6H_4$	$C_6H_5\text{-}CH_2$	198-200	507 (4.26)
<u>6.5</u>	$2\text{-}CN\text{-}4\text{-}NO_2\text{-}C_6H_3$	$n\text{-}C_4H_9$	261	559 (4.31)
<u>6.6</u>	$2\text{-}CN\text{-}4\text{-}NO_2\text{-}C_6H_3$	$n\text{-}C_{12}H_{25}$	263	566 (4.31)
<u>6.7</u>	$2\text{-}CN\text{-}4\text{-}NO_2\text{-}C_6H_3$	C_6H_5	199-201	557 (4.30)
<u>6.8</u>	$2\text{-}CN\text{-}4\text{-}NO_2\text{-}C_6H_3$	$C_6H_5\text{-}CH_2$	289	550 (4.28)
<u>6.9</u>	$2,4(NO_2)_2\text{-}C_6H_3$	$n\text{-}C_4H_9$	301-03	547 (4.30)
<u>6.10</u>	$2,4(NO_2)_2\text{-}C_6H_3$	$n\text{-}C_{12}H_{25}$	271	548 (4.30)
<u>6.11</u>	$2,4(NO_2)_2\text{-}C_6H_3$	C_6H_5	249	534 (4.28)
<u>6.12</u>	$2,4(NO_2)_2\text{-}C_6H_3$	$C_6H_5\text{-}CH_2\text{-}$	189 (188)[2]	532 (4.28)
<u>6.13</u>	$4\text{-}Cl\text{-}C_6H_4$	$n\text{-}C_4H_9$	217-19	454 (4.20)
<u>6.14</u>	$4\text{-}Cl\text{-}C_6H_4$	$n\text{-}C_{12}H_{25}$	312	456 (4.21)
<u>6.15</u>	$4\text{-}Cl\text{-}C_6H_4$	C_6H_5	267	448 (4.19)
<u>6.16</u>	$4\text{-}Cl\text{-}C_6H_4$	$C_6H_5\text{-}CH_2$	249-51	447 (4.18)

2. *Properties of the prepared 1-arylazo-substituted 2- and 4-naphthylsulfides **5** and **6***

All the prepared 1-arylazo-substituted 2- and 4-naphthylsulfides **5** and **6** have been characterized by their elementary analytical data.

Several representatives have also been studied by ^{1}H-NMR spectroscopy. As can be seen from Chart 1 for the compounds **5.1** and **6.1**, the measured chemical shifts are in complete agreement with the given structure.

A characteristic feature of all the prepared arylazo-substituted naphthylsulfides **5** and **6** is their deep colour which results, as can be seen from Tables III and IV, from a long-wavelength absorption band, the maximum of which is centered depending on the substituents in the aryl moiety between 440 and 560 nm.

Furthermore, some compounds are easily soluble in non-polar or weakly polar organic solvents. This property is due to the absence of ionogenic groups in the molecular framework of the arylazo-substituted naphthyl sulfides **5** and **6** and the presence of long-chained S-linked alkyl groups in several derivatives.

The high solubility of the obtained 1-arylazo-substituted 2- and 4-naphthylsulfides **5** and **6** in organic solvents stimulated us to check their order parameters **S** and dichroic ratios **D** in liquid crystalline materials. As can be seen from Table V, due to their sufficient solubility in the nematic system and their vast flat molecular structure, all compounds studied exhibit relatively high dichroic ratios **D** and rather good order parameters **S**. Thus, the studied 1-arylazo-substituted 2- and 4-naphthylsulfides **5** and **6** can be used, similarly to other arylazo compounds[9] or aromatic sulfides,[10] as guest-compounds for enhancing the contrast of liquid-crystalline host materials. Further detailed studies in this direction are in progress.

TABLE V

Dichroic ratio (D) and order parameter (S) of several elected 4-arylazo-1-naphthylsulfides **6** at their absorption maxima measured in the nematic liquid crystal mixture CLF104A containing 2 wt% of the corresponding dye at 25°C

No.	max (in CLF104A)	D[a])	S[b])
6.1	541	9.28	0.72
6.2	545	9.30	0.73
6.3	540	9.09	0.71
6.4	539	9.09	0.71
6.5	572	9.26	0.72
6.6	575	9.29	0.73
6.7	555	9.09	0.71
6.8	552	9.09	0.71

[a] Dichroic ratio $D = \varepsilon_{\parallel}/\varepsilon_{\perp}$.

[b] Order parameter $S = (D - 1)/(D + 2)$.

TABLE VI

Elementary analysis of the prepared 2- and 4-arylazosubstituted 1-naphthylsulfides **5** and **6**, resp. (cald./found)

No.	MW	formula	C	H	N	S	Cl
5.1	365	$C_{20}H_{19}N_3O_2S$	65.75 65.57	5.20 5.29	11.50 11.99	8.76 8.50	
5.2	477	$C_{28}H_{35}N_3O_2S$	70.44 70.65	7.33 7.40	8.80 8.69	6.70 6.65	
5.3	385	$C_{22}H_{15}N_3O_2S$	68.57 68.43	3.89 3.72	10.90 11.04	8.31 8.52	
5.4	399	$C_{23}H_{17}N_3O_2S$	69.17 69.22	4.26 4.11	10.52 10.41	8.02 8.29	
5.5	390	$C_{21}H_{18}N_4O_2S$	64.61 64.43	4.61 4.70	14.35 14.42	8.20 8.01	
5.6	502	$C_{29}H_{34}N_4O_2S$	69.32 69.10	6.77 6.81	11.15 11.34	6.37 6.49	
5.7	410	$C_{23}H_{14}N_4O_2S$	67.31 67.02	3.41 3.55	13.65 13.42	7.80 7.95	
5.8	424	$C_{24}H_{16}N_4O_2S$	67.92 68.13	3.77 3.51	13.20 13.19	7.54 7.66	
5.9	410	$C_{20}H_{18}N_4O_4S$	58.53 58.79	4.39 4.21	13.65 13.39	7.80 7.92	
5.10	522	$C_{28}H_{34}N_4O_4S$	64.36 64.69	6.51 6.23	10.72 10.76	6.13 6.05	
5.11	430	$C_{22}H_{14}N_4O_4S$	61.39 61.47	3.25 3.17	13.02 13.19	7.44 7.31	
5.12	444	$C_{23}H_{16}N_4O_4S$	62.16 62.33	3.60 3.72	12.61 12.38	7.20 7.21	
5.13	354	$C_{20}H_{19}N_2SCl$	67.79 67.59	5.36 5.22	7.90 7.33	9.03 9.72	10.01 9.87
5.14	432	$C_{28}H_{35}N_2SCl$	77.77 77.12	8.10 8.23	6.48 6.77	7.40 7.91	8.20 8.51
5.15	340	$C_{22}H_{15}N_2SCl$	77.64 77.21	4.41 4.62	8.23 8.82	9.41 9.24	10.42 10.23
5.16	354	$C_{23}H_{17}N_2SCl$	77.96 78.21	4.80 4.97	7.90 7.33	9.03 9.31	10.01 10.21

TABLE VI (*continued*)

No.	MW	formula	C	H	N	S	Cl
6.1	365	$C_{20}H_{19}N_3O_2S$	65.75 65.77	5.20 5.29	11.50 11.99	8.76 8.90	
6.2	477	$C_{28}H_{35}N_3O_2S$	70.44 70.75	7.33 7.30	8.80 8.99	6.70 6.55	
6.3	385	$C_{22}H_{15}N_3O_2S$	68.57 68.33	3.89 3.92	10.90 10.84	8.31 8.52	
6.4	399	$C_{23}H_{17}N_3O_2S$	69.17 69.32	4.26 4.11	10.52 10.44	8.02 8.22	
6.5	390	$C_{21}H_{18}N_4O_2S$	64.61 64.33	4.61 4.80	14.35 14.22	8.20 8.11	
6.6	502	$C_{29}H_{34}N_4O_2S$	69.32 69.00	6.77 6.91	11.15 11.32	6.37 6.51	
6.7	410	$C_{23}H_{14}N_4O_2S$	67.31 67.02	3.41 3.55	13.65 13.42	7.80 7.95	
6.8	424	$C_{24}H_{16}N_4O_2S$	67.92 68.03	3.77 3.51	13.20 13.19	7.54 7.66	
6.9	410	$C_{20}H_{18}N_4O_4S$	58.53 58.89	4.39 4.21	13.65 13.29	7.80 7.92	
6.10	522	$C_{28}H_{34}N_4O_4S$	64.36 64.70	6.51 6.23	10.72 10.66	6.13 6.15	
6.11	430	$C_{22}H_{14}N_4O_4S$	61.39 61.87	3.25 3.11	13.02 13.13	7.44 7.21	
6.12	444	$C_{23}H_{16}N_4O_4S$	62.16 62.43	3.60 3.82	12.61 12.48	7.20 7.11	
6.13	354	$C_{20}H_{19}N_2SCl$	67.79 67.89	5.36 5.52	7.90 7.41	9.03 9.12	
6.14	432	$C_{28}H_{35}N_2SCl$	77.77 77.44	8.10 8.34	6.48 6.57	7.40 7.51	
6.15	340	$C_{22}H_{15}N_2SCl$	77.64 77.51	4.41 4.72	8.23 8.42	9.41 9.20	
6.16	354	$C_{23}H_{17}N_2SCl$	77.96 77.21	4.80 4.97	7.90 8.33	9.03 9.41	

EXPERIMENTAL

All melting points were estimated by a heating table microscope and were corrected. The absorption spectra were measured in dimethylformamide at a concentration of 1×10^{-5} mol/l using a M40 UV/VIS spectrophotometer from Carl Zeiss Jena.

The starting arylazo-substituted chloronaphthalenes **3** and **4** were synthesized by the reaction of the appropriate substituted arylazo-naphthols **1** and **2**, available by an usual coupling reaction of a diazonium salt with the desired coupling component, according to the procedure described in Reference 8, with $POCl_3$ in dimethyl formamide according to Reference 8 and recrystallized from methanol.

All compounds prepared were checked by means of elementary analysis. The data obtained are summarized in Table VI.

The dichroic ratio **D** and order parameter **S** have been measured in a cell consisting of two parallel arranged glass plates filled with the pure liquid crystalline mixture CLF104A as reference-cell and with a mixture of CLF104A and 2 wt% of the corresponding dye as measure-cell, resp.

1-Arylazo-substituted 2- and 4-naphthylsulfides **5** *and* **6**. A solution of 3g of the corresponding arylazo-substituted chloronaphthalenes **3** or **4** in 50 ml of dimethylformamide was mixed with 20 ml of the appropriate mercaptide and heated in the presence of trimethyl amine at about 100°C. The reaction extent was monitored by TLC and was stopped by cooling and addition of acetic acid to the reaction mixture. The reaction product precipitated was isolated by suction and purified by recrystallization from acetic acid (method A) or by column chromatography on silica gel (using a mixture of toluene/methanol 9:1 as eluent) and recrystallized from acetic acid (method B).

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